





International Conference on Thermoelectrics June 2005 Clemson, South Carolina

presented by

T. Caillat

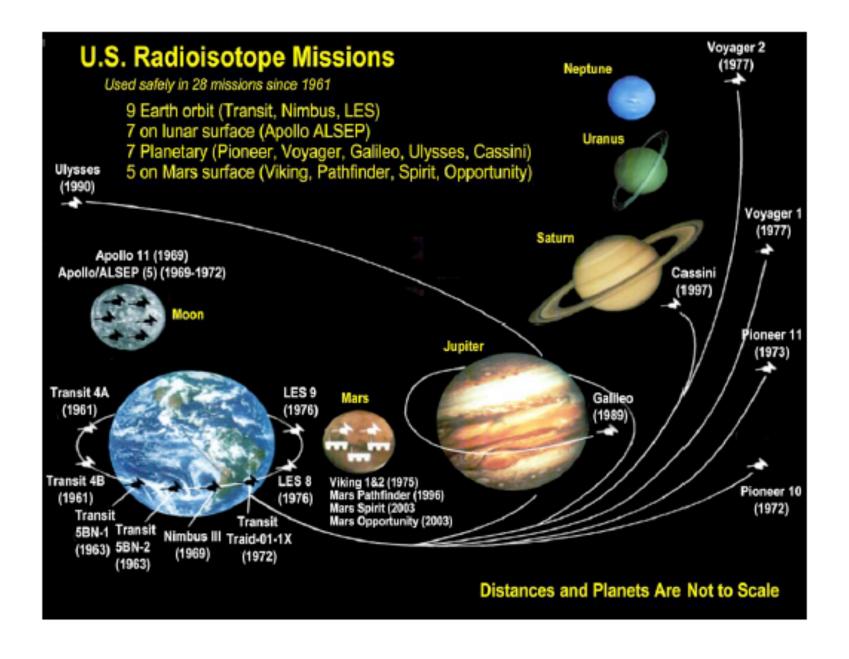
J. Sakamoto, A. Jewell, J. Cheng, J. Paik, F. Gascoin, J. Snyder, R. Blair, C. -K. Huang, J. -P. Fleurial

Jet Propulsion Laboratory/California Institute of Technology



U.S. missions using radioisotopes power and/or heating sources

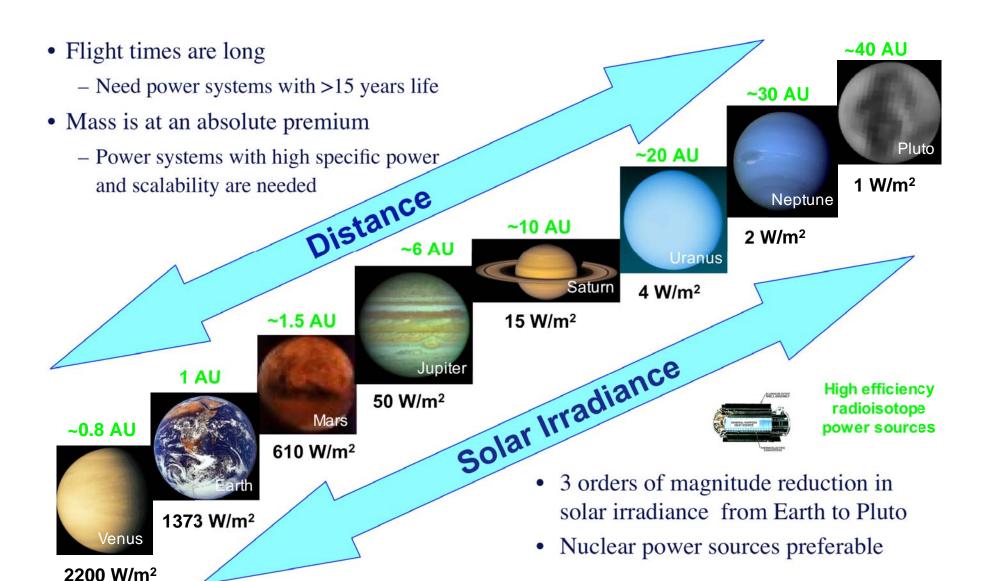






Power Technology

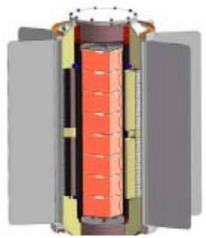




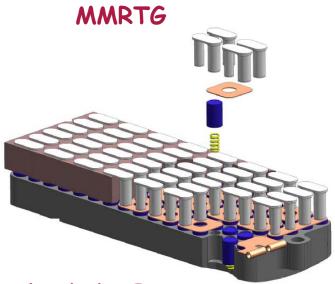












Spring-loaded TE converter

ltem/Converter	PbTe/TAGS MMRTG
Hot side temperature (K)	823
Cold side temperature (K)	483
Converter efficiency (%)	7.6
System efficiency (%)*	6.4
Thermal power (BOM)(W _{th})	2000
Thermal efficiency (%)	
Electrical power (BOM) (W _e)	125.3
Number of GPHS modules	8
Total PuO ₂ mass (kg)	5.02
Total system mass estimate (kg)	43.8
Specific power estimate (W _e /kg)	2.85

Fe Cup_

N-Leg

Fe Cup

P-Leg Fe Cold Cap

-TAGS

PbSnTe

Ni Hot Shoe

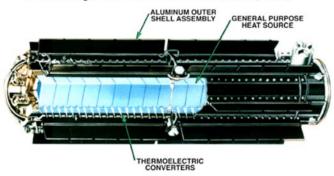


General Purpose Heat Source RTG



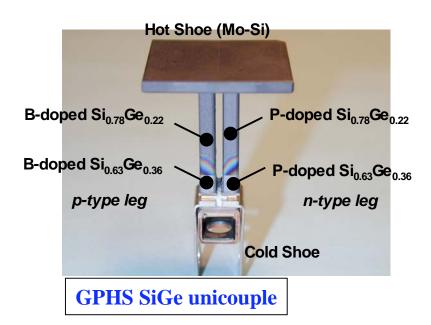
General Purpose Heat Source (GPHS)

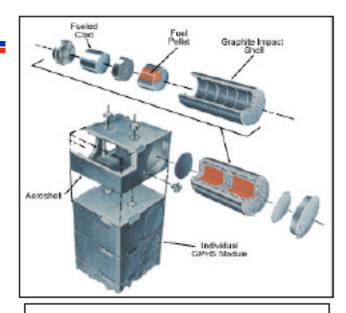
Radioisotope Thermoelectric Generator (RTG)



- POWER OUTPUT 285 W(e)
- FUEL LOADING 4400 W(t); 132,500 Ci
- WEIGHT 124 lbs
- SIZE 16.6 in x 44.5 in

The three Radioisotope Thermoelectric Generators (RTGs) provide electrical power for Cassini's instruments and computers. They are being provided by the U.S. Department of Energy.





General Purpose Heat Source Module

GPHS-RTG Performance Data

Power output-We	290 beginning of life 250 end of life
Operational life - hrs	40,000 after launch
Weight-kg	55.5
Output voltage	28
Dimensions	42.2 diameter 114 long
Hot junction temperature-K	1270
Cold junction temperature-K	566
Fuel	PuO ₂
Thermoelectric material	SiGe
Numbers of unicouples	572
Mass of Pu-238-g	7,561

Advanced Radioisotope Power Systems (APRS) for NASA missions



Overall objective:

Develop low mass, high efficiency, low-cost Advanced Radioisotope Power System with double the Specific Power and Efficiency over state-of-the-art Radioisotope Thermoelectric Generators (RTGs)

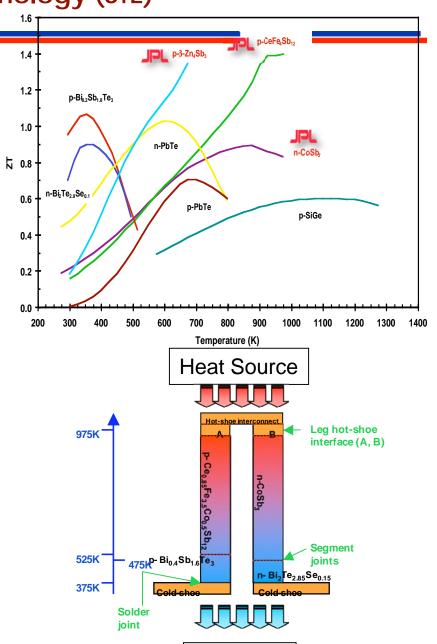


Segmented Thermoelectric Technology (STE)



- New high ZT materials
 - Development initiated in 1991 and supported by ONR and DARPA
 - Higher efficiency values
- Segmented unicouples
 - Large ∆T, high ZT -> high efficiency
 - Using a combination of state-of-the-art TE materials (Bi₂Te₃-based materials) and new, high ZT materials developed at JPL
 - Skutterudites : CeFe₄Sb₁₂ and CoSb₃
 - Zn₄Sb₃
 - Current materials operation limited to ~ 975K
 - Higher average ZT values
 - Higher material conversion efficiency
 - → Up to 15 % for a 300-975K temperature gradient

Efficiency
$$\eta = \frac{T_H - T_C}{T_H} \frac{\sqrt{I + ZT - 1}}{\sqrt{I + ZT} + \frac{T_C}{T_H}}$$

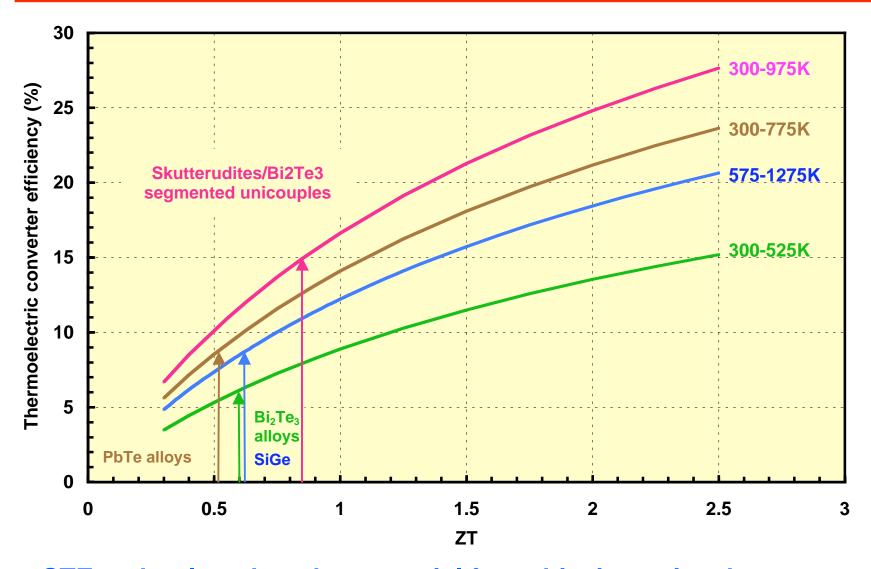


Heat Sink



Converter efficiency: state-of-the-art vs. segmented thermoelectric technology

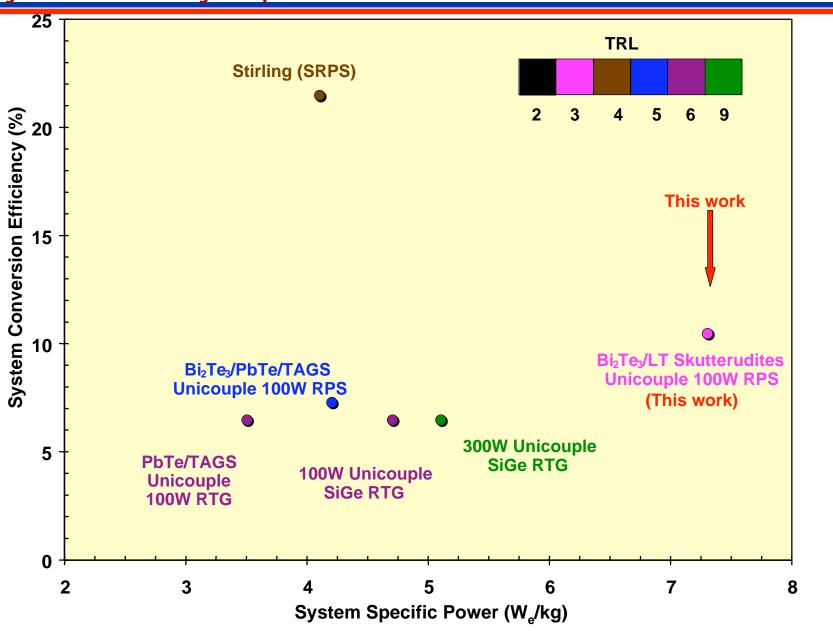




STE technology has the potential for achieving twice the converter efficiency of SOA thermoelectrics



System Efficiency & Specific Power: STE vs. SOA

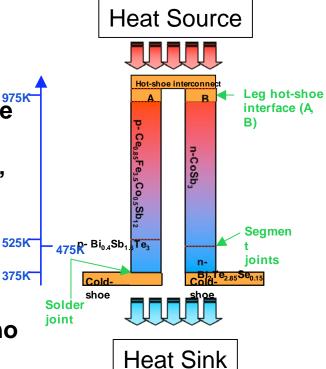


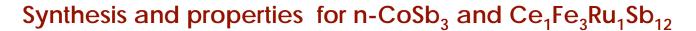


JPL

STE-ARPS

- Would use advanced materials segmented legs
- •700 to 100°C operation
- Current GPHS-RTG unicouple design would be mostly conserved
- Modifications required to radiator fins to accommodate for lower rejection temperature
- Shorter housing
- New segmented unicouples could "replace" unicouples almost "one for one"
- Advantages of thermoelectrics
 - Flight proven, long life demonstrated
 - Solid state energy conversion -> reliability, no vibration, no moving parts
 - Scalable
 - No single point failure
 - Significant system heritage







Synthesis

- ♦ Melting (~1200C in BN crucibles) and milling in steel vials under Argon
- ♦ Hot pressing at temperatures between 600 and 700C, graphite dies, 20,000 psi
- Developed 100g batch process for n-type and p-type
- Overall process similar to SOA thermoelectrics; powder metallurgy process easily scalable to larger quantities

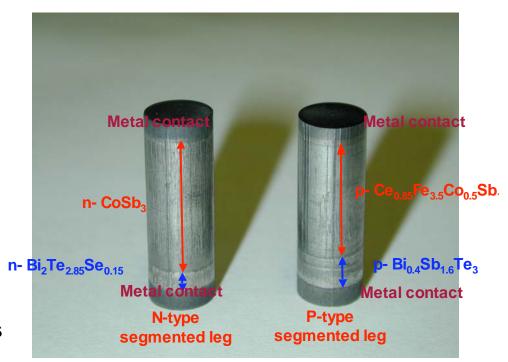
Properties

- N-type CoSb₃
 - Uses Pd, Te (~ 1at% each) as dopants to optimize carrier concentration
 - CTE: 9.1 x 10⁻⁶K
 - Decomposition temperature: 878C
- Ce_{0.85}Fe_{3.5}Co_{0.5}Sb₁₂
 - CTE: 12.1 x 10⁻⁶K
 - Decomposition temperature: 778C
- Mechanical property measurements in progress





- Developed uniaxial hot-pressing technique for legs fabrication
 - Powdered materials stacked on the top of each other
 - Temperature optimized → density
 close to theoretical value
 - In graphite dies and under argon atmosphere
 - With metallic diffusion barriers
 between the thermoelectric materials
 - Metallic contacts at hot- and coldside
 - Low electrical resistance bonds (<5µ
 Ωcm²) achieved → negligible impact
 on overall unicouple performance



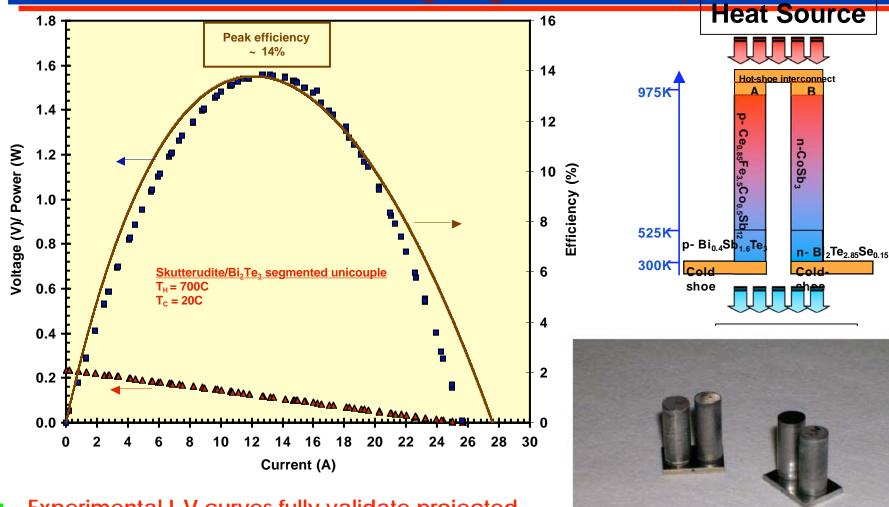




Skutterudite unicouples fabricated by

diffusion bonding

Thermal and electrical testing - Segmented unicouple



- Experimental I-V curves fully validate projected performance
 - Translate into ~ 14% efficiency for 975K-300K
 ΔT
- Results independently confirmed at the University of New Mexico



Sublimation Suppression November 2004



- Completed in-gradient experiment on an n-an p-type leg pressed at 535C and bonded to a Mo plate
 - A single p-leg (6 mm long) was bonded to a Mo plates
 - Tested in 700C-100C gradient for 7 days with a 4mm thick, machined, titania opacified/150 mg/cc aerogel donut
 - Post cross-sectional analysis showed that: both the leg and the aerogel indicated that there were no signs of significant sublimation (no noticeable depletion bands in the leg and no condensation inside the aerogel or on the inner wall of the ampoule



Single skutterudite leg bonded to a Mo hot-shoe



Bonded legs with machined aerogel donuts



In-gradient test set-up



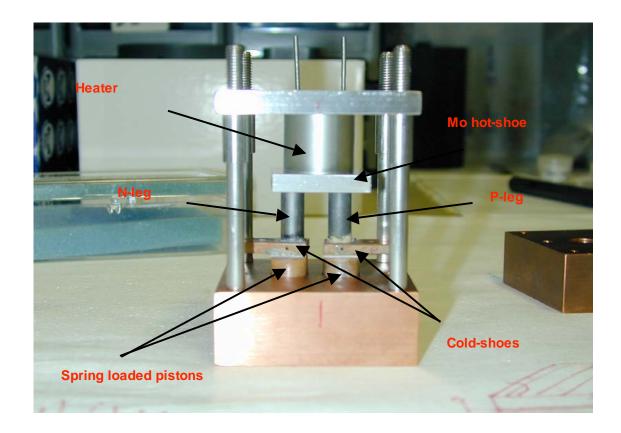
SEM picture of cross section near the Mo/leg interface after 7 days at 700C: no sublimation was observed



Photograph of aerogel donut cut in half after 7 days at 700C in contact with skutterudite leg: no sublimation deposit was observed



■ Fabricated 1st generation spring loaded test fixtures



P- and n-skutterudite legs mounted in spring loaded test fixture



Lifetime performance demonstration elements

THERMOELECTRIC PROPERTIES (FY04)

Examples:

- SiGe: dopant precipitation
- Fine grained SiGe: grain growth
- TAGS: compositional change

Testing:

Coupons

Impact:

• Change in efficiency, P output

Solution:

• Composition, doping control

MATERIALS SUBLIMATION (FY04)

Examples:

- · SiGe: Si & Ge
- TAGS, PbTe: Te, Se, Ag, Sb
- Skutterudites: Sb

Testing:

Coupons

Impact:

 A/I, porosity, contact resistance, mechanical failure

Solution:

- Encapsulation, coatings
- More refractory materials

THERMAL INSULATION (FY05-06)

Examples:

• Si in MFI

Testing:

• Unicouple

Impact:

- Shorting
- Contamination

Solution:

Processing and engineering control

THERMO-MECHANICAL INTEGRITY (FY05-06)

Testing:

Unicouple

Impact:

- Contact resistance
- Mechanical failure

Solution:

Device engineering/modeling

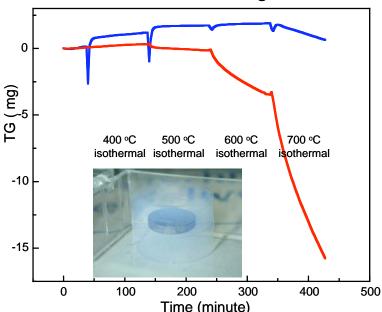
LIFETIME MODEL

FUEL DECAY



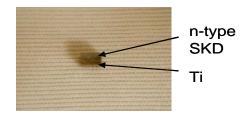
iblimation Suppression with Aerogel Encapsulation

n-SKD with aerogel encapsulationn-SKD without aerogel

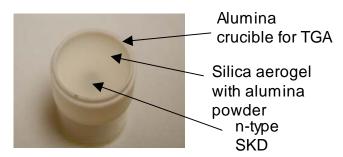


Time (minute)			
Sample	Temperature	Sublimation rate in vacuum (~ 2 ×10 ⁻⁶ Torr)	
n-SKD without aerogel	500 °C	5.31 × 10 ⁻⁴ g/cm ² hr	
	600 °C	5.16 × 10 ⁻³ g/cm ² hr	
	700 °C	2.15 × 10 ⁻² g/cm ² hr	
n-SKD with aerogel encapsulation	500 °C	<u>-</u>	
	600 °C	-	
	700 °C	2.70 × 10 ⁻³ g/cm ² hr	

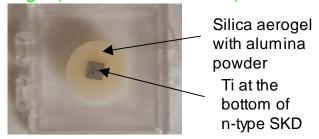
n-SKD cube (3 mm×3 mm×1.7mm) for the sublimation test



n-SKD cube encapsulated with aerogel (before sublimation test)



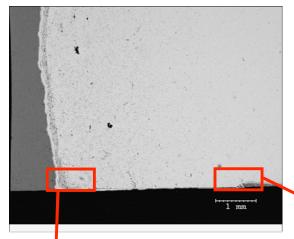
Bottom view of n-SKD cube encapsulated with aerogel (after sublimation test)

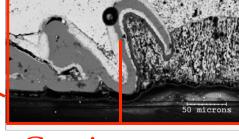




Ti coated-type tested in-gradient for 20 days

975K _____

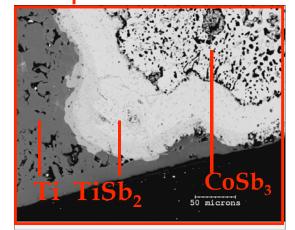






Coating stops

N-type Ti coated skutterudite leg



No apparent degradation after 20 days

CoSb₃

CoSb₂

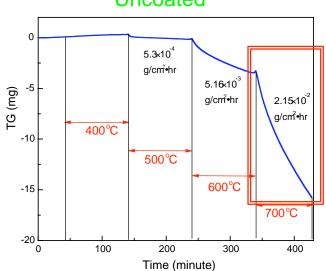
CoSb

- Metal junction still intact
- Significant improvement over uncoated

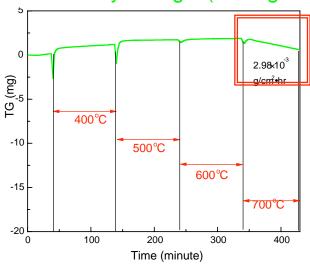


Aerogel and Ti/Mo Coatings Significantly Reduce Sublimation at ROI

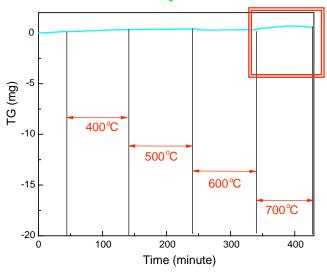
Uncoated



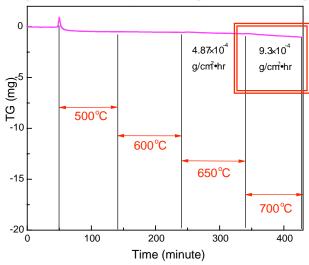
Low Density Aerogel (50 mg/cm³)



Titanium/Molybdenum Foil



Higher Density Aerogel (100 mg/cm³)





Skutterudite materials temperature stability/performance optimization: Ce₁Fe_{4-x}Ru_xSb₁₂ system



	Composition	Decomposition temperature
DGF277	Ce ₁ Fe ₄ Sb ₁₂	760.6 °C
NSKP5	Ce ₁ Fe ₃ Ru ₁ Sb ₁₂	830.7 °C
NSKP6	Ce ₁ Fe ₂ Ru ₂ Sb ₁₂	850.6 °C
NSKP10	Ce ₁ Fe ₁ Ru ₃ Sb ₁₂	955.8 °C
NSKP11	Ce ₁ Ru ₄ Sb ₁₂	994.3 °C

[⇒] Results indicate increasing decomposition temperature trend with increasing Ru concentration





Sublimation rates from TGA measurement in dynamic vacuum

High temperature skutterudite sublimation rates at beginning of test

	Sublimation rate of n-SKD (IrSb ₃)	Sublimation rate of p-SKD (CeRu ₄ Sb ₁₂)	
600 °C	3.88 × 10 ⁻⁵ (g/cm²·hr)	1.32 × 10 ⁻⁴ (g/cm²·hr)	
700 °C	9.61 × 10 ⁻⁴ (g/cm²·hr)	7.91 × 10 ⁻⁴ (g/cm ² ·hr)	
800 °C	3.92 × 10 ⁻³ (g/cm²·hr)	1.65 × 10 ⁻³ (g/cm²·hr)	
900 °C	1.66 × 10 ⁻² (g/cm ² ·hr)	1.05 × 10 ⁻² (g/cm ² ·hr)	

Skutterudite sublimation rates at beginning of test

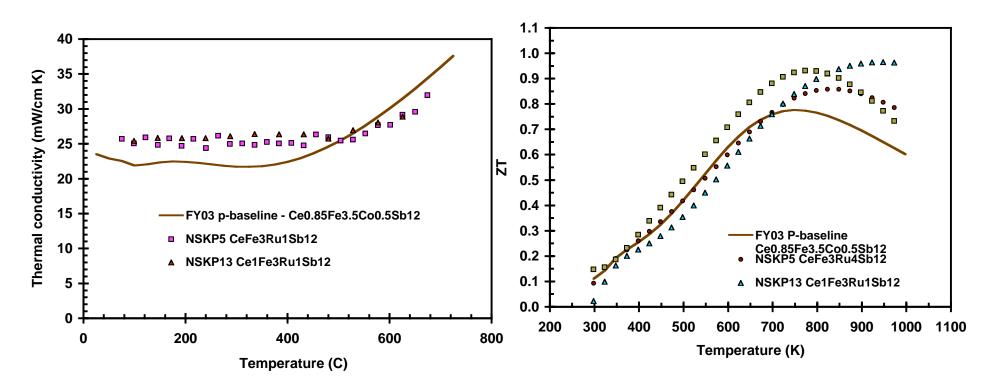
	Sublimation rate of n-SKD	Sublimation rate of baseline p-SKD (Ce _{0.85} Fe _{3.5} Co _{0.5} Sb ₁₂)	Sublimation rate of new p-SKD (Ce ₁ Fe ₃ Ru ₁ Sb ₁₂)
500 °C	5.31 × 10 ⁻⁴	7.40 × 10 ⁻⁴	1.70 × 10 ⁻⁴
	(g/cm ² ·hr)	(g/cm ² ·hr)	(g/cm²·hr)
600 °C	5.16 × 10 ⁻³	6.78 × 10 ⁻³	4.12 × 10 ⁻⁴
	(g/cm ² ·hr)	(g/cm ² ·hr)	(g/cm²·hr)
700°C	2.15 × 10 ⁻²	2.80 × 10 ⁻²	1.40 × 10 ⁻³
	(g/cm ² ·hr)	(g/cm²·hr)	(g/cm²·hr)

Decreasing sublimation rates





Thermal conductivity and ZT versus temperature for p-type materials

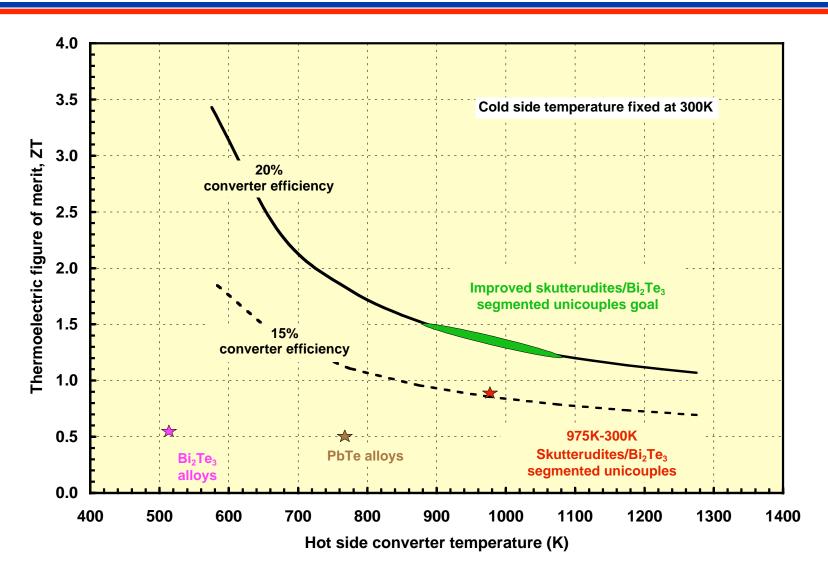


Developed second generation p-type CeFe₃Ru₁Sb₁₂TE material that possesses improved ZT and higher temperature stability (1100K) than Ce_{0.85}Fe_{3.5}Co_{0.5}Sb₁₂ baseline material





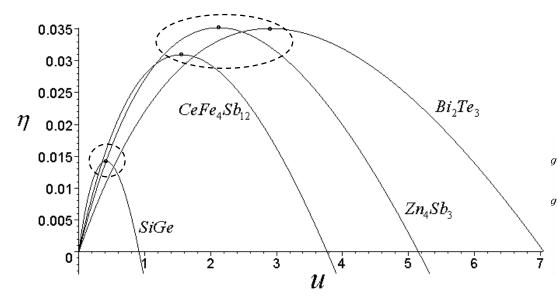
Achieving 20% Converter efficiency



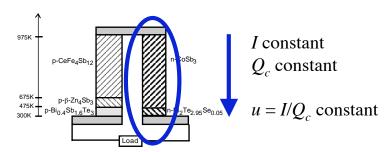


E Device Configuration: Segmenting vs Cascading

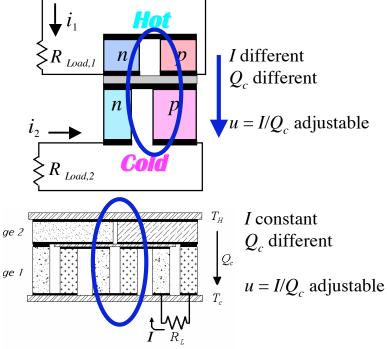
- Segmented Thermoelectric
 - constrained by constant current
 - $u = I/Q_c$
 - u ≈ Constant
- Cascaded Thermoelectric
 - independent circuits for each stage
 - Current different in each stage
 - Heat different in each leg
 - u optimized for each stage



Segmented TE Generator



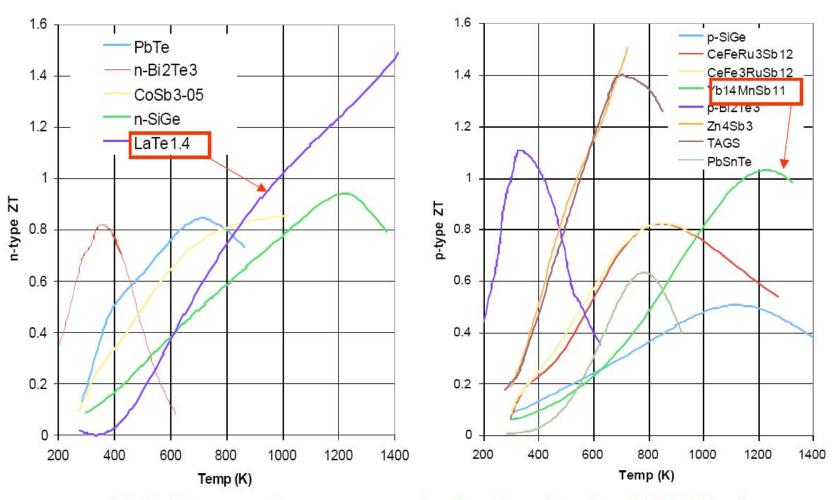
Cascaded TE Generators









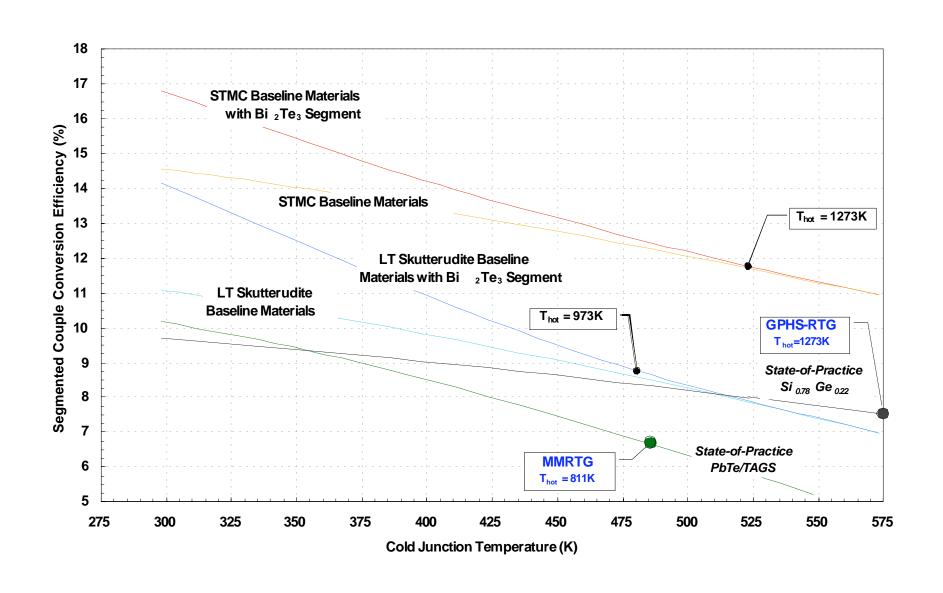


High-T materials are currently developed under STMC Task





Advanced Materials Thermoelectric Conversion Efficiency

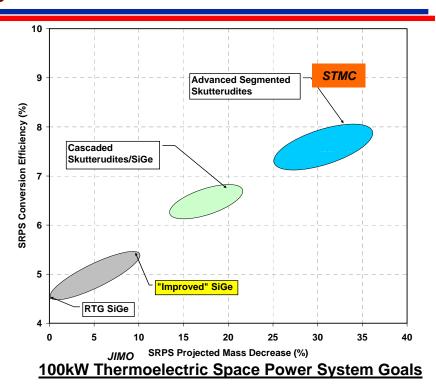




Potential High Power Thermoelectric Converter Technology Development for Future High Power Science Missions



- Segmented Thermoelectric Multicouple Converter (STMC) technology for 100 kWe class power systems
- Primary objective is technology development based on high performance advanced thermoelectric materials for potential future NASA missions
 - 2x increase in conversion efficiency
 - High rejection temperature (600-700K)
 - Limit size of heat rejection system
 - And minimize overall system mass
- Scope focused on:
 - Power Conversion System design and modeling
 - Advanced TE materials evaluation and optimization
 - Advanced TE Couple Array engineering development
 - Scale-up converter fabrication
 - Planning for technology insertion



Projected Performance Improvements using Advanced TE Materials over SiGe Alloys used in RTGs

STMC TE Technology Development Team

- Jet Propulsion Laboratory
- Boeing/Rocketdyne
- Teledyne Energy Systems
- University of Michigan
- Michigan State University
- University of South Florida

- University of California at Davis
- Clemson University
- Princeton University
- Cornell University
- University of Southern California
- University of New Mexico



High Power TE Converter Technology Development Challenges



- Technical risk reduction associated with high power conductively coupled thermoelectric (TE) power conversion systems
 - Highly compact, modular, conductively coupled TE converter technology compatible with large scale production
 - Performance compatible with wide range of heat source and heat rejection operating temperatures
 - High reliability throughout fabrication process and during operation (> 15 years)

Key activities include:

- Application of advanced thermal/mechanical/electrical modeling tools to develop converter design, fabrication and assembly that will result in maximum thermoelectric performance and lifetime
- Large scale synthesis of high performance TE materials and fabrication of TE couples
- Development of innovative large scale fabrication and assembly technology for TE couple arrays and converter assemblies
- Extensive materials, components and sub-scale converter assembly testing
- Lifetime performance prediction and validation through accelerated testing at the component and sub-scale converter assembly level



Thermoelectric Converter Enhancements



Planned improvements to fabrication and performance of conductively coupled Thermoelectric SiGe couple stack developed for SP-100

Improved TE Materials (increase conversion efficiency up to 10%)

Low contact resistance interconnects

(From 35-50 to less than 25 $\mu\Omega$.cm² at 1275K)

Refractory Aerogel for superior thermal insulation and ease of module/TCA assembly (no glass between couple legs or around legs)

Module arrangement facilitates interconnection
(all handled from exterior SP-100 Multicouple (8-couple series))

of TCA)

- HOT SIDE -HIGH VOLTAGE INSULATOR COMPL1 25 NIOBIUM LOW PRESSURE ELECTRODES PERIMETER GLASS T/E COUPLES ITERCO<u>N</u>NECT COMPLIANT PAD .00025 NIOBIUM .050 Nb FILAMENTS .005 NIOBIUM HIGH VOLTAGE INSULATOR -COLD SIDE -

Thick compliant pads and graphite layers reduced/eliminated to reduce waste ∆T from 30% to 5–10% (compliance achieved through structural engineering)

TE couples arranged in modules to facilitate fabrication, assembly and ensure lifetime

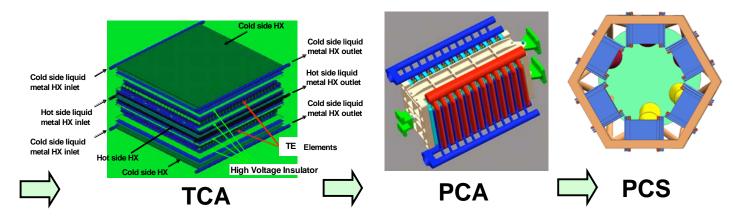
Detailed thermal/mechanical/fractural analysis for robust design that will survive fabrication, assembly and operation







- TE is a modular technology that requires three discrete assemblies
 - Metallized TE legs
 - High voltage insulator/interconnect assembly
 - Heat exchanger assembly
- Bonding the three assemblies utilizes the same technology regardless of the assembly size
 - 2x2 and 2x4 mini TCA modules
 - 1/8 Sub-scale TCA modules
 - Thermoelectric Converter Assembly (TCA)
 - Power Converter Assembly (PCA)
- The fabrication technology is cost effective
 - Critical technology development is done at the smallest module level
 - TCA and PCA fabrication is directed at large assemblies issues



TE Module





STMC High Temperature TE Materials Effort

High Temperature *n*-type

 La_2Te_3 published zT = 1.3Needs to be reproduced

Half Heusler

Clathrates

Skutterudites

High Temperature *p*-type

Greatest development need

 $Cu_2Mo_6Se_8 zT = 0.6$

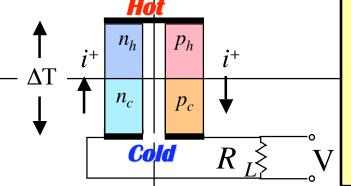
Zintl

Clathrates

Skutterudites



- ◆ Goal to achieve ZT >1.0 within 1275-700K
 - Minimum goal: 0.85
 - Compatible with Skutterudites
 - Thermal & mechanical stability
- ♦ Down selection in March 2005



low Temperature *n*-type

Skutterudite

 $CoSb_3$ today zT = 0.8

 ACo_4Sb_{12} goal zT = 1.1

low Temperature p-type

Skutterudite

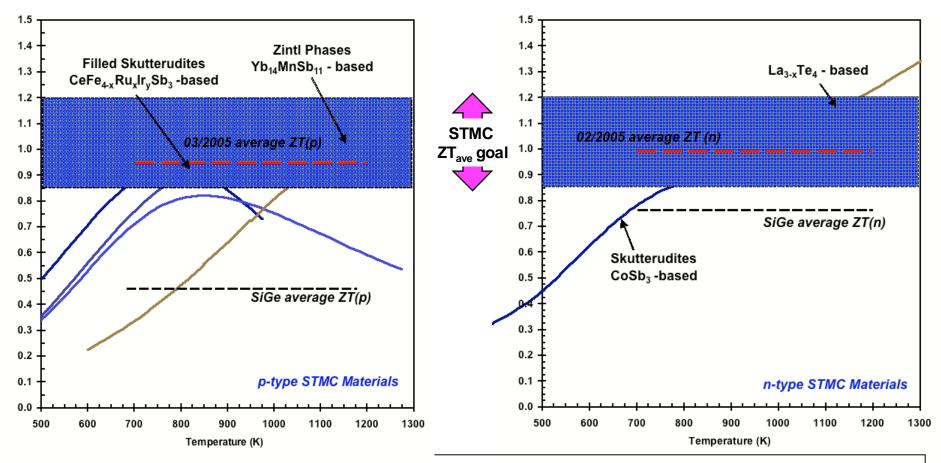
 $CeFe_4Sb_{12}$ today zT = 1.1

 $CeFe_4Sb_{12}$ goal zT = 1.4





STMC Advanced TE Materials Status



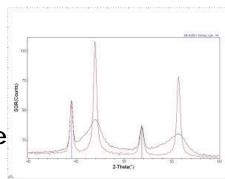
- As of 05/2005, STMC combined p/n TE materials performance exceeds minimum goal of average ZT = 0.85 across 1200K-700K temperature differential
- Average ZT value of 0.95 about 50% better than that of SiGe alloys used in GPHS-RTG
- Materials downselect for high temperature STMC scheduled for late May 2005

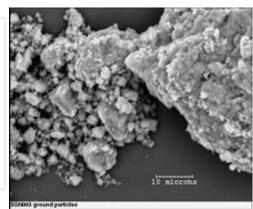




Large Scale Synthesis of TE Materials

- Developed powder metallurgy techniques that can be scaled up to industrial quantities
- Selected use of mechanical alloying followed by hot pressing to synthesize Si_{0.8}Ge_{0.2} alloys
 - Follows technology development initiated by Ames Laboratory in the early 1990s
 - Process is simpler, highly reproducible and less costly than one used in past SiGe programs
- High temperature pressure sintering for skutterudites
 - Segmented TE technology
- Developed scaled up synthesis of TE leg compacts for producing large numbers of legs
 - From 12.5 to 40 mm diameter compacts
 - HIP process also under evaluation













Low Contact Resistance TE/Interconnect Leg Bond

- Contact resistance between TF materials and current electrodes was one of remaining issues in SP-100 program
 - Low resistance, stable contact must be formed
 - All prior technology focused on developing All prior technology focused on developing contacts after synthesis of the TE materials

 Best solution developed under SP-100 was complex

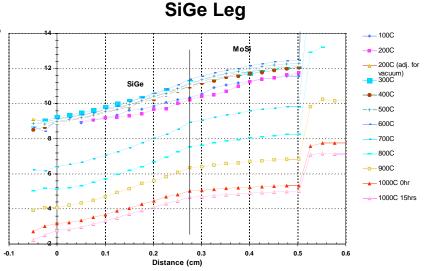
 SiCo Ma / Co Ma / Craphito M/ foil multilayer contacts after synthesis of the TE materials
 - SiGe/Mo/Ge/Mo/Graphite/W foil multilayer
 - Did not fully meet goal of $< 25 \mu\Omega$.cm² required for multicouple technology
- Achieved very low contact resistance values
 - For both SiGe and skutterudites
 - Less than 5 μΩ.cm²
 - Bond achieved during direct leg fabrication
 - Low contact resistance bond, thermally stable
 - Fewer fabrication and assembly steps
 - Easy scale up
 - Electrical and mechanical life performance tests planned

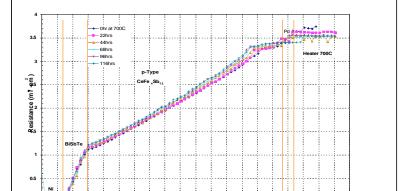


Mo-capped SiGe leg



Ti-capped Skutterudite leg





Segmented TE Leg

Contact Resistance Measurements

Distance (cm)



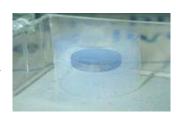


Sublimation and Thermal Insulation

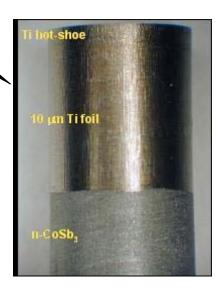
- Sublimation issue is TE material dependent
 - Testing to establish rates are under way
 - Aerogel is found effective and reduces rates to minimum (x100 lower rates)
 - Aerogel shows only minimal linear shrinkage below 1275K and has a much lower thermal conductivity than the glass used for SP-100
 - Metal coatings are also effective and have been extensively tested (sublimation eliminated)
 - Likely to use combination of both

Uncoated TE material: beginning of life sublimation rate at operating temperature (g/cm² hr) TAGS at 775K ~ 1 Low Temperature n-Skutterudites $\sim 2.15 \times 10^{-2}$ (SKD) at 975K Low Temperature p-Skutterudites $\sim 1.4 \times 10^{-3}$ (SKD) at 975K $\sim 3.66 \times 10^{-3}$ Chevrels (M_xMo₆Se₈) at 1275K LaYbTe, at 1275K $\sim 2.11 \times 10^{-4}$ SiGe at 1275K $\sim 4.8 \times 10^{-5}$

Aerogel: More than 100 times lower rates







Metal coating: full sublimation suppression







Key Structural Integrity Issues

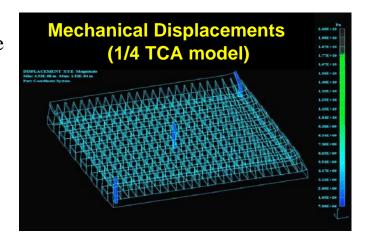
- Coefficient of thermal expansion mismatches within TE device stack, and between stack and large heat exchangers
- "Bowing" of thermoelectric legs due to large ΔT
- Surviving fabrication and assembly steps and operation

- Reviewed preliminary design of STMC and TCA

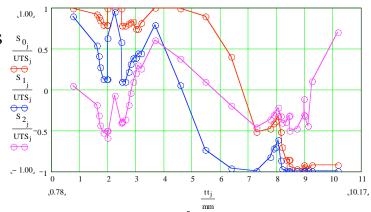
- Key goal is to redistribute thermally induced stresses by selecting optimal materials combinations, element geometries
 - Optimized for steady-state operating conditions
 - Comparing models for SP-100 SiGe-based converter and STMC
 - Developed a rapid evaluation tool using an elastic model of the HT-TMC that allows to compare trends
- Secondary objective is to minimize parasitic losses (ΔT across non-TE layers and fill factor thermal losses)
 - Initial calculations show only 10% losses (about 30% for SP-100)

Mechanical tests of TE samples

- 4-point bend data obtained on skutterudites and SiGe (comparable values at room temperature)
- Testing and modeling of interface fracture toughness and development of fail-safe structures



Elastic Stress Model of ½ STMC Stack
Red Line – Heat Exchanger Held Rigidly
Blue Line – Free to Expand but no Bending
Purple Line – Free to expand and bend



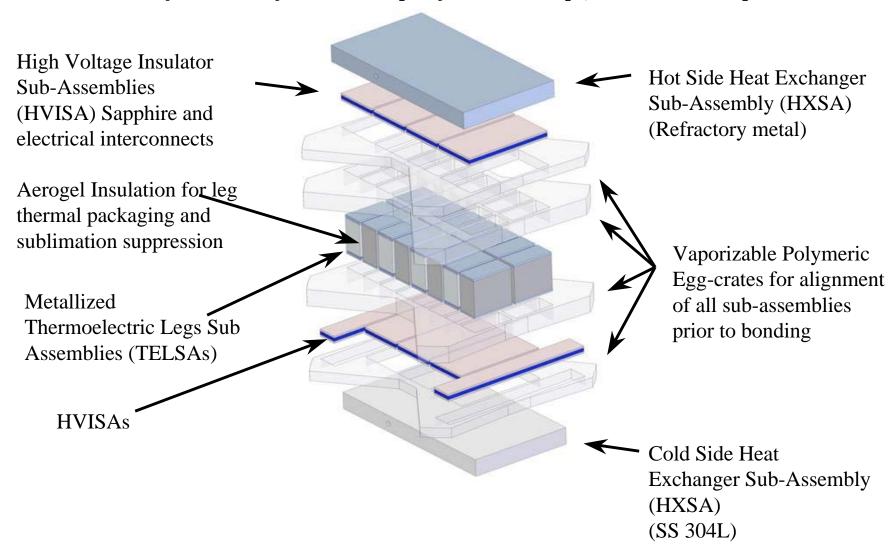
Fraction of Ultimate Strain VS Distance in mm



STMC Module



STMC Module fabrication: fewer and simpler fabrication steps, scalable to mass production

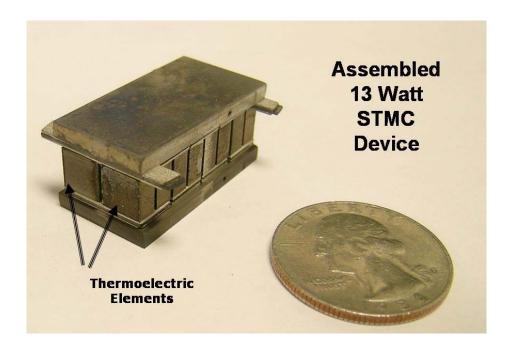




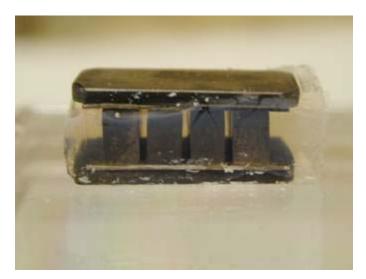


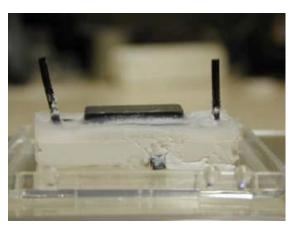
JPL

LT-TMC Technology Demonstration Completed in May 2005



LT-TMC Teledyne Module #2 975K – 425K Operation, 13W





LT-TMC JPL Module #1 975K – 425K Operation, 5W